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On the Action of Papain Enzyme. (VII)

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19. Studies on Acetylene and its Derivatives. (XIII)

Preparation of Caprolactam from Propargyl Alcohol. (1)

Sango KUNICHIKA, Shinzaburo OKA and Tomikazu YOSHIKAWA

(Nodzu Laboratory)

According to the following scheme, we have been trying the preparation of caprolactam.

$$2CH\equiv C\cdot CH_2OH + 1/2O_2 \xrightarrow[NH_4Cl]{Cu_2Cl_2} HOCH_2-C\equiv C-C\equiv C\cdot CH_2OH$$

$$\xrightarrow[+4H_2]{\text{Raney Ni}} HO(CH_2)_6OH \xrightarrow[-2H_2]{\text{Cu, Cr}} \text{(cyclic ether)} \xrightarrow{NH_3} \text{(cyclic amide)}$$

In this paper, the oxidative coupling of propargyl alcohol to hexadiynediol, using air or oxygen and a cuprous salt as catalyst, and its hydrogenation to hexanediol are described.

A shaking stainless steel autoclave of 300 c.c. capacity was filled with a mixture of 60g. H_2O, 19g. NH_4Cl, 6g. Cu_2Cl_2 and pure propargyl alcohol. Air or oxygen was pressed to 10~20 atm. After the reaction was over, the contents of the autoclave were filtered, the solid washed with a possible minimum amout of water and dissolved in 10 times methanol. Removing the insoluble materials, the methanol solution of hexadiynediol was hydrogenated with 40 atm. hydrogen at 10~20°, in the presence of Ranney nickel catalyst. The anti-catalytic action of copper ions could be eliminated by addition of a small amount of zinc dust.

The yields of hexanediol boiling at 110°/4mm., melting at 40~41° were 50~60 % of the theoretical amounts based on the propargyl alcohol used. Using pure hexadiynediol melting at 112° which was recrystallized from methanol or water, 94 % yield of hexanediol was obtained.

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20. On the Action of Papain Enzyme. (VII)

Masashichi YOSHIOKA

(Ogiu Laboratory)

It was formerly reported that Rongalite makes papain enzyme active in protein decomposition.

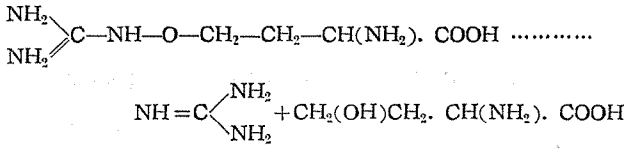
Later, a study was made on the type of the active group by which papain enzyme resolves protein, and as the result, a -CHO group was reconnized.

Investigations were made as to under what mechanism this active group exists in the papain molecule where by any free -CHO group could hardly be recognized. Such being the case, the present author carried on his study on the active group, under the assumption of the presence of Type I (-$\overset{|}{C}$H-O-$\overset{|}{C}$-) and II (-NH-O-$\overset{|}{C}$H-).

As for Type I, it has already been proven as in the report IV.

This time, Canavanine was used to examine Type II. At first, the *Rf* value was sought by the paper chromatographic method ; the following chemical change was not recognized ;

Canavanine *Rf* 0.296
Canavanine + Rongalite *Rf* 0.299
Guanidine *Rf* 0.463



Further, the optical density was measured by the Beckmann Spectrophotometer, and the results are as in the following tables.

Type II was not recognized in these results.

Table 1. Optical density.

225-300 mμ	Substance		
	Canavanine (100γ/cc)	Rongalite (50γ/cc)	Guanidin (25γ/cc)
225	—	0.020	—
230	1.400	0.015	—
235	0.818	0.009	—
240	0.416	0.004	0.225
245	0.205	0.003	0.041
250	0.085	0.005	−0.003
255	0.035	0.008	−0.010
260	0.014	0.010	−0.010
265	0.009	0.011	−0.010
270	0.008	0.010	−0.009
275	0.008	0.009	−0.009
280	0.007	0.009	−0.009
285	0.007	0.008	−0.009
290	0.007	0.008	−0.008
295	0.007	0.007	−0.006
300	0.007	0.006	−0.006

Table 2. Optial density (Canavanine+Rongalite).

225-300 mμ	Hour of Acetone				
	0	24	48	72	120
225	1.370	—	—	1.628	1.130
230	0.670	1.878	1.840	1.228	0.702
235	0.300	1.106	1.070	0.648	0.420
240	0.125	0.540	0.520	0.334	0.217
245	0.063	0.236	0.220	0.155	0.113
250	0.037	0.096	0.083	0.070	0.065
255	0.022	0.042	0.037	0.039	0.043
260	0.021	0.021	0.022	0.026	0.033
265	0.020	0.015	0.014	0.020	0.026
270	0.021	0.013	0.013	0.017	0.023
275	0.021	0.014	0.014	0.017	0.023
280	0.021	0.015	0.015	0.018	0.022
285	0.021	0.017	0.017	0.018	0.022
290	0.021	0.018	0.018	0.018	0.021
295	0.021	0.020	0.020	0.018	0.020
300	0.021	0.021	0.022	0.019	0.021

The experimental results so far obtained have led the author to the belief in Type I combination.

Therefore, by adding activator such as Rongalite which affect papain molecule, -CHO group is considered to appear, and it is the active group that resolves protein.

21. Studies on the Phosphatase in Takadiastase

Senji UTZINO and Ryokuero SUZUE

(Utzino Laboratory)

We tried to separate the phosphatase in Takadiastase, using the dialysed Takadiastase solution as an original enzyme solution. As substrate, 0.2 ml. of 1% sodium β-glycerophosphate (GP-ase), 0.5% sodium pyrophosphate (PP-ase) or 0.012 *M* Na_4-ATP (ATP-ase) solution was used. 1) As for the influence of pH of 0.5 *M* acetate or 0.1 *M* veronal buffer solution, the pH curves of GP-ase, PP-ase and ATP-ase activity were all observed to be similar. 2) Among metallic ions, Mg or Ca ion increased, or at least did not reduce, these phosphatase activities, whereas Zn or Mn ion inhibited their activities. 3) When enzyme solutions were kept at 50°, 60°, 70° or 80°C for 10 mins., their activites were strongly damaged at 60°C and completely at 80°C. 4) The original enzyme solution was adsorbed by the same volume of $Al(OH)_3$